

# Asymptotic Correction Schemes for Semilocal Exchange-Correlation Functionals

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Aiming to remedy the incorrect asymptotic behavior of conventional semilocal exchange-correlation (XC) density functionals for finite systems, we propose an asymptotic correction (AC) scheme, wherein an exchange density functional whose functional derivative has the correct  $(-1/r)$  asymptote can be directly added to any semilocal density functional. In contrast to semilocal density approximations, our resulting exchange kernel in reciprocal space exhibits the desirable singularity of the type  $O(-1/q^2)$  as  $q \rightarrow 0$ , which is a necessary feature for describing the excitonic effects in non-metallic solids. By applying this scheme to a popular semilocal density functional, PBE [J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)], the prediction of properties that are sensitive to the asymptote, such as the highest occupied molecular orbital energies and Rydberg excitation energies, is significantly improved, while the prediction of properties that are insensitive to the asymptote, such as reaction energies and valence excitation energies, remains essentially the same as PBE. In addition, without loss of accuracy, two closely related AC schemes are developed for the efficient treatment of large systems.

Over the past two decades, Kohn-Sham density functional theory (KS-DFT) [1] has been one of the most powerful theoretical methods for the ground-state properties of large electronic systems. Its time-dependent extension, time-dependent density functional theory (TDDFT) [2–4] has gradually become popular for the study of excited-state and time-dependent properties.

In KS-DFT, the exact exchange-correlation (XC) density functional  $E_{xc}[\rho]$  remains unknown and needs to be approximated. Accurate density functional approximations to  $E_{xc}[\rho]$  have been successively developed to extend the applicability of KS-DFT to a wide range of systems. Despite the recent advances in the orbital-dependent density functional approach [5], semilocal density functionals remain popular due to their computational efficiency for large systems and reasonable accuracy for applications governed by short-range XC effects [6]. However, due to the associated several qualitative failures, semilocal functionals can produce erroneous results in situations where the accurate treatment of non-locality of the XC hole is important [7–9].

One of the important and long-standing subjects in KS-DFT is the asymptotic behavior of the XC potential  $v_{xc}(\mathbf{r}) = \delta E_{xc}(\mathbf{r})/\delta \rho(\mathbf{r})$ . For finite systems, the exact  $v_{xc}(\mathbf{r})$  is known to exhibit the correct Coulombic  $(-1/r)$  decay as  $r \rightarrow \infty$  [10–13]. However, due to the severe self-interaction error [14], the XC potentials derived from conventional semilocal functionals fail to describe the correct asymptotic behavior, yielding qualitatively incorrect predictions for properties where the asymptotic region of the XC potential is crucially important, such as the vertical ionization potentials and high-lying (Rydberg) excitation energies of atoms and molecules [15, 16].

Without resorting to the expensive orbital-dependent density functional approach, currently, perhaps the most

popular approach in practice to improve the asymptote of the XC potential is the model XC potential approach [17–25], wherein an asymptotically corrected XC potential is directly modeled. However, as a number of popular model potentials are found *not* to be functional derivatives, these model potentials are not variationally stable, and the associated XC energies are not uniquely defined. Therefore, properties obtained from these model potentials need to be carefully interpreted [26].

By contrast, for a system of  $N$  electrons, the Fermi-Amaldi (FA) XC functional [27],

$$E_{xc}^{\text{FA}}[\rho] = -\frac{1}{2N} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (1)$$

which is just  $(-1/N)$  times the Hartree energy functional, appears to be the simplest XC functional whose functional derivative has the correct  $(-1/r)$  asymptote. However, there are several problems with the use of the FA model [28]. While the FA XC potential is correct in the asymptotic region, it is inaccurate elsewhere. Besides, due to its delocalized XC hole, the FA model is not size-consistent, where the energy of a system composed of two or more well-separated subsystems is *not* identical to the sum of the energies of the separate subsystems [29].

In this Letter, we propose an asymptotic correction (AC) scheme for any system composed of atoms (e.g., atoms, molecules, and solids), wherein a modified FA XC functional, which is size-consistent in the calculated energy and whose functional derivative has the correct  $(-1/r)$  asymptote, can be directly added to any semilocal functional. Without loss of accuracy, two related efficient schemes are also developed for large systems.

By partitioning and localizing a modified FA XC hole to the atoms in a system, we propose the “localized” FA

(LFA) exchange functional,

$$E_x^{\text{LFA}}[\rho_\alpha, \rho_\beta] = - \sum_{\sigma=\alpha,\beta} \sum_A \frac{1}{2N_{A,\sigma}} \times \iint \rho_{A,\sigma}(\mathbf{r}) \rho_{A,\sigma}(\mathbf{r}') \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (2)$$

to resolve the size-inconsistency issue associated with the FA model [30]. Here the second sum is over all the atoms in the system,  $\rho_{A,\sigma}(\mathbf{r})$  is the  $\sigma$ -spin ( $\sigma = \alpha$  for spin up or  $\beta$  for spin down) electron density associated with the atom  $A$ ,

$$\rho_{A,\sigma}(\mathbf{r}) = w_A(\mathbf{r}) \rho_\sigma(\mathbf{r}), \quad (3)$$

and the weight function  $w_A(\mathbf{r})$ , ranging between 0 and 1, is of the Hirshfeld type [31, 32]:

$$w_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r})}{\sum_B \rho_B^0(\mathbf{r})}, \quad (4)$$

where  $\rho_A^0(\mathbf{r})$  is the spherically averaged electron density computed for the isolated atom  $A$ .  $N_{A,\sigma}$  is the number of the  $\sigma$ -spin electrons associated with the atom  $A$ ,

$$N_{A,\sigma} = \int \rho_{A,\sigma}(\mathbf{r}) d\mathbf{r}, \quad (5)$$

and the long-range interelectron repulsion operator  $\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)/|\mathbf{r} - \mathbf{r}'|$  is to retain the correct asymptotic behavior without the (unneeded) energy contribution from the complementary short-range operator, where  $\omega$  is a parameter defining the range of the operators. Due to the sum rule of  $\sum_A w_A(\mathbf{r}) = 1$ , we have  $\sum_A \rho_{A,\sigma}(\mathbf{r}) = \sum_A w_A(\mathbf{r}) \rho_\sigma(\mathbf{r}) = \rho_\sigma(\mathbf{r})$  and  $\sum_A N_{A,\sigma} = N_\sigma$  (the number of  $\sigma$ -spin electrons).

By taking the functional derivative of  $E_x^{\text{LFA}}[\rho_\alpha, \rho_\beta]$ , the LFA exchange potential for  $\sigma$ -spin electrons is

$$\begin{aligned} v_{x,\sigma}^{\text{LFA}}(\mathbf{r}) &= \frac{\delta E_x^{\text{LFA}}[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma(\mathbf{r})} \\ &= - \sum_A \frac{w_A(\mathbf{r})}{N_{A,\sigma}} \int \rho_{A,\sigma}(\mathbf{r}') \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \end{aligned} \quad (6)$$

In the asymptotic limit,  $v_{x,\sigma}^{\text{LFA}}(\mathbf{r})$  has the correct asymptotic form,

$$\begin{aligned} \lim_{r \rightarrow \infty} v_{x,\sigma}^{\text{LFA}}(\mathbf{r}) &= - \sum_A \frac{w_A(\mathbf{r})}{N_{A,\sigma}} \int \rho_{A,\sigma}(\mathbf{r}') \frac{1}{|\mathbf{r}|} d\mathbf{r}' \\ &= - \sum_A \frac{w_A(\mathbf{r})}{N_{A,\sigma}} \frac{1}{r} N_{A,\sigma} \\ &= - \frac{1}{r} \sum_A w_A(\mathbf{r}) = - \frac{1}{r}. \end{aligned} \quad (7)$$

From Eqs. (2) and (6), we have

$$E_x^{\text{LFA}}[\rho_\alpha, \rho_\beta] = \frac{1}{2} \sum_{\sigma=\alpha,\beta} \int \rho_\sigma(\mathbf{r}) v_{x,\sigma}^{\text{LFA}}(\mathbf{r}) d\mathbf{r}, \quad (8)$$

which shows that the LFA exchange energy density per electron also has the correct  $(-1/2r)$  asymptote [17, 33].

For calculations of excitation energies from adiabatic linear-response TDDFT [4], the functional derivative of  $v_{x,\sigma}^{\text{LFA}}(\mathbf{r})$  is taken to give the LFA exchange kernel for  $\sigma$ -spin electrons,

$$\begin{aligned} f_{x,\sigma}^{\text{LFA}}(\mathbf{r}, \mathbf{r}') &= \frac{\delta v_{x,\sigma}^{\text{LFA}}(\mathbf{r})}{\delta \rho_\sigma(\mathbf{r}')} = \frac{\delta^2 E_x^{\text{LFA}}[\rho_\alpha, \rho_\beta]}{\delta \rho_\sigma(\mathbf{r}) \delta \rho_\sigma(\mathbf{r}')} \\ &= - \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \sum_A \frac{w_A(\mathbf{r}) w_A(\mathbf{r}')}{N_{A,\sigma}}. \end{aligned} \quad (9)$$

In contrast to semilocal density approximations, the LFA exchange kernel in reciprocal space has the correct long-wavelength  $O(-1/q^2)$  divergence as  $q \rightarrow 0$ , which is crucially important for the proper description of excitonic effects in non-metallic solids [34–37]. We emphasize that this striking feature appears naturally from our fully non-local LFA exchange functional.

To improve its description of short-range XC effects, the LFA exchange functional is combined with a popular semilocal functional, PBE [38]. However, this will produce a double-counting (DC) energy  $E_{\text{DC}}$ , which needs to be removed. As a significant fraction of the LFA exchange energy should be from the core regions of atoms, we presuppose that  $\rho_{A,\sigma}(\mathbf{r})$  is *strictly localized* at  $\mathbf{R}_A$  (the position of atom  $A$ ) in Eq. (2), which gives  $\rho_{A,\sigma}(\mathbf{r}) \approx N_{A,\sigma} \delta(\mathbf{r} - \mathbf{R}_A)$  for satisfying Eq. (5), to estimate  $E_{\text{DC}}$ ,

$$\begin{aligned} E_{\text{DC}} &= - \sum_{\sigma=\alpha,\beta} \sum_A \frac{1}{2N_{A,\sigma}} \\ &\times \iint \left\{ N_{A,\sigma} \delta(\mathbf{r} - \mathbf{R}_A) \right\} \left\{ N_{A,\sigma} \delta(\mathbf{r}' - \mathbf{R}_A) \right\} \\ &\times \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &= - \sum_{\sigma=\alpha,\beta} \sum_A \frac{1}{2N_{A,\sigma}} (N_{A,\sigma})^2 \left\{ \lim_{\mathbf{r} \rightarrow \mathbf{R}_A} \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{R}_A|)}{|\mathbf{r} - \mathbf{R}_A|} \right\} \\ &= - \sum_{\sigma=\alpha,\beta} \sum_A \frac{1}{2N_{A,\sigma}} (N_{A,\sigma})^2 \left\{ \frac{2\omega}{\sqrt{\pi}} \right\} \\ &= - \frac{\omega}{\sqrt{\pi}} \sum_{\sigma=\alpha,\beta} \sum_A N_{A,\sigma} = - \frac{\omega}{\sqrt{\pi}} N. \end{aligned} \quad (10)$$

This estimate is very accurate for systems with highly localized charges (e.g., HCl), and less accurate for systems with delocalized charges (e.g., benzene) [30]. Our resulting LFA-PBE functional is given by

$$E_{xc}^{\text{LFA-PBE}} = E_{xc}^{\text{PBE}} + E_x^{\text{LFA}} - E_{\text{DC}}. \quad (11)$$

Note that  $v_{x,\sigma}^{\text{DC}}(\mathbf{r}) = \delta E_{\text{DC}} / \delta \rho_\sigma(\mathbf{r}) = -\omega / \sqrt{\pi}$  is simply a constant. As the KS potential is only defined within an arbitrary constant, without loss of generality, we require

the KS potential to vanish asymptotically, which gives  $v_{x,\sigma}^{\text{DC}}(\mathbf{r}) = 0$ . Unlike the FA model, LFA-PBE is size-consistent for any system composed of atoms [30]. Note that LFA-PBE (with  $\omega = 0$ ) reduces to PBE.

For systems composed of many atoms, LFA-PBE can be computationally unfavorable due to the numerical integration of many Hartree-like potentials in  $v_{x,\sigma}^{\text{LFA}}(\mathbf{r})$ . To resolve this computational bottleneck without loss of much accuracy,  $v_{x,\sigma}^{\text{LFA}}(\mathbf{r})$  can be efficiently evaluated based on the resolution-of-identity (RI) approximation [39, 40]. Following Ref. [40],  $\rho_{A,\sigma}(\mathbf{r})$  is first expanded with an auxiliary basis set  $\{g_p(\mathbf{r})\}$ ,

$$\rho_{A,\sigma}(\mathbf{r}) \approx \tilde{\rho}_{A,\sigma}(\mathbf{r}) = \sum_p a_p g_p(\mathbf{r}), \quad (12)$$

where the expansion coefficients  $\{a_p\}$  are given by Eq. (8) of Ref. [40] (with  $\rho(\mathbf{r})$  being replaced by  $\rho_{A,\sigma}(\mathbf{r})$ ). The RILFA exchange potential is evaluated by

$$v_{x,\sigma}^{\text{RILFA}}(\mathbf{r}) = - \sum_A \frac{w_A(\mathbf{r})}{N_{A,\sigma}} \int \tilde{\rho}_{A,\sigma}(\mathbf{r}') \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (13)$$

From Eq. (10) of Ref. [40] (with the Hartree energy being replaced by the LFA exchange energy), the RILFA exchange energy is given by

$$E_x^{\text{RILFA}} = \sum_{\sigma=\alpha,\beta} \sum_A \left\{ - \frac{1}{N_{A,\sigma}} \times \iint \rho_{A,\sigma}(\mathbf{r}) \tilde{\rho}_{A,\sigma}(\mathbf{r}') \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{1}{2N_{A,\sigma}} \iint \tilde{\rho}_{A,\sigma}(\mathbf{r}) \tilde{\rho}_{A,\sigma}(\mathbf{r}') \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right\}. \quad (14)$$

For a sufficiently large auxiliary basis set, the RILFA scheme approaches to the LFA scheme. Here, we define RILFA-PBE by Eq. (11), with  $E_x^{\text{LFA}}$  being replaced by  $E_x^{\text{RILFA}}$ .

For very large systems, both the LFA and RILFA schemes may be impractical, compared to semilocal functionals. Aiming to retain the correct  $(-1/r)$  asymptote with essentially no added computational cost relative to semilocal functionals, we define the LFAs exchange potential  $v_{x,\sigma}^{\text{LFAs}}(\mathbf{r})$  (“s” refers to “strict”), by presupposing the *strict* localization of  $\rho_{A,\sigma}(\mathbf{r})$  at  $\mathbf{R}_A$  in  $v_{x,\sigma}^{\text{LFA}}(\mathbf{r})$  (i.e.,  $\rho_{A,\sigma}(\mathbf{r}) \approx N_{A,\sigma} \delta(\mathbf{r} - \mathbf{R}_A)$ ),

$$v_{x,\sigma}^{\text{LFAs}}(\mathbf{r}) = - \sum_A \frac{w_A(\mathbf{r})}{N_{A,\sigma}} \times \int \left\{ N_{A,\sigma} \delta(\mathbf{r}' - \mathbf{R}_A) \right\} \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (15)$$

$$= - \sum_A w_A(\mathbf{r}) \frac{\text{erf}(\omega |\mathbf{r} - \mathbf{R}_A|)}{|\mathbf{r} - \mathbf{R}_A|}.$$

The asymptote of  $v_{x,\sigma}^{\text{LFAs}}(\mathbf{r})$  is easily shown to be correct,

$$\lim_{r \rightarrow \infty} v_{x,\sigma}^{\text{LFAs}}(\mathbf{r}) = - \sum_A w_A(\mathbf{r}) \frac{1}{|\mathbf{r}|} = - \frac{1}{r}. \quad (16)$$

Based on Eq. (8), the LFAs exchange energy is given by

$$E_x^{\text{LFAs}} = \frac{1}{2} \sum_{\sigma=\alpha,\beta} \int \rho_{\sigma}(\mathbf{r}) v_{x,\sigma}^{\text{LFAs}}(\mathbf{r}) d\mathbf{r}, \quad (17)$$

to retain the correct  $(-1/2r)$  asymptote of the LFAs exchange energy density per electron. Although  $v_{x,\sigma}^{\text{LFAs}}(\mathbf{r})$  differs from the functional derivative of  $E_x^{\text{LFAs}}$  by a factor of 2, the prescribed LFAs scheme approaches to the LFA scheme for a sufficiently small  $\omega$  value, where  $v_{x,\sigma}^{\text{LFAs}}(\mathbf{r})$  becomes an excellent approximation of  $v_{x,\sigma}^{\text{LFA}}(\mathbf{r})$ . Similarly, LFAs-PBE is defined by Eq. (11), with  $E_x^{\text{LFA}}$  being replaced by  $E_x^{\text{LFAs}}$ .

For the exact KS-DFT, the minus HOMO energy of a molecule should be the same as the vertical ionization potential (IP) of the molecule [10, 11, 41–43]. Therefore, the optimal  $\omega$  values for LFA-PBE, RILFA-PBE, and LFAs-PBE are determined by fitting the predicted IPs (calculated by the minus HOMO energies) of 18 atoms and 113 molecules in the IP131 database to the corresponding experimental IPs [44]. All calculations are performed with a development version of Q-Chem 3.2 [45], using the 6-311++G(3df,3pd) basis set (and sufficiently large auxiliary basis sets for the RILFA scheme), unless noted otherwise. The error for each entry is defined as (error = theoretical value – reference value).

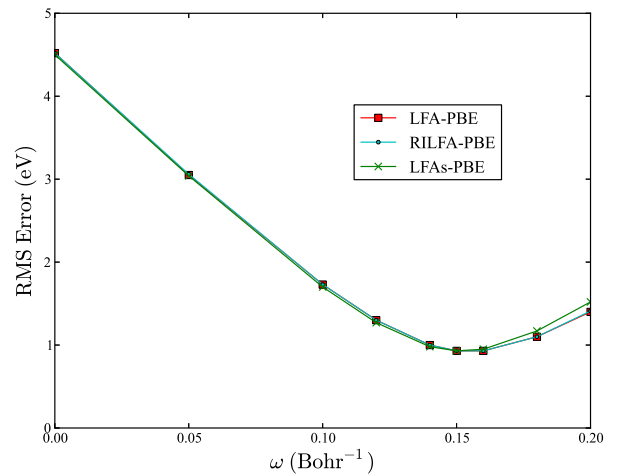


FIG. 1. The root-mean-square (RMS) errors of the IP131 database [44], for LFA-PBE, RILFA-PBE, and LFAs-PBE at different values of  $\omega$ . The  $\omega = 0$  case corresponds to PBE.

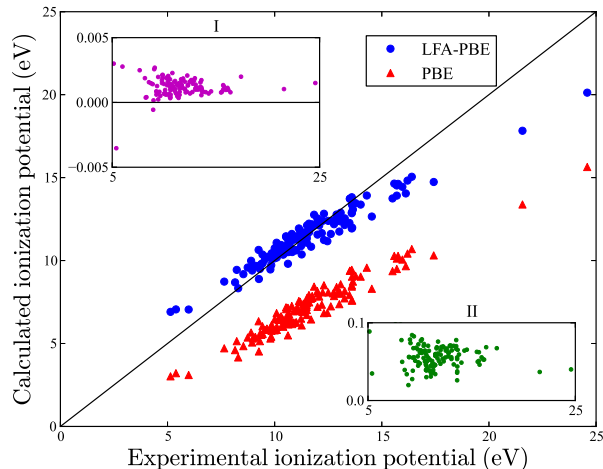


FIG. 2. Calculated versus experimental ionization potentials (IPs) for the IP131 database [44]. Inset I shows the differences between the IPs calculated by RILFA-PBE and LFA-PBE, while inset II shows the differences between the IPs calculated by LFAs-PBE and LFA-PBE. For the LFA schemes,  $\omega = 0.15 \text{ Bohr}^{-1}$  is adopted.

As shown in Fig. 1, the minimum root-mean-square (RMS) errors of the IP131 database, for LFA-PBE, RILFA-PBE, and LFAs-PBE all occur at  $\omega = 0.15 \text{ Bohr}^{-1}$ , where the RMS errors associated with the LFA-corrected PBE functionals are more than three times smaller than the RMS error associated with PBE (the  $\omega = 0$  case), reflecting the importance of the correct asymptote of XC potential for the accurate prediction of IPs [30].

Adopting  $\omega = 0.15 \text{ Bohr}^{-1}$  for the LFA schemes, the calculated IPs are plotted against the experimental values in Fig. 2. As can be seen, the differences between the IPs calculated by RILFA-PBE and LFA-PBE are within 0.005 eV, and the differences between the IPs calculated by LFAs-PBE and LFA-PBE are within 0.1 eV. Therefore, the LFA-corrected PBE functionals yield very similar results, which implies that their XC potentials should be very similar [30]. By contrast, the predicted IPs of PBE are seriously underestimated, due to the incorrect asymptote.

Similar results are found, when our LFA schemes are combined with LDA [46, 47]. As both the LDA and PBE XC potentials decay exponentially in the asymptotic region, their predicted IPs remain similar, requiring essentially the same corrections from the LFA schemes (i.e., with the same optimal  $\omega$ ) [30]. Therefore,  $\omega = 0.15 \text{ Bohr}^{-1}$  can be recommended as the optimal  $\omega$  value, when the LFA schemes are combined with a local or semilocal functional whose functional derivative has the (incorrect) exponential asymptote.

The performance of the LFA schemes is also examined

TABLE I. Mean absolute errors (in kcal/mol) of the reaction energies of 30 chemical reactions [48], calculated by the PBE and LFA-corrected PBE functionals ( $\omega = 0.15 \text{ Bohr}^{-1}$ ). (1 kcal/mol = 0.0434 eV = 0.00159 hartree.)

System	PBE	LFA-PBE	RILFA-PBE	LFAs-PBE
Reaction (30)	4.38	4.48	4.47	4.42

TABLE II. Mean absolute errors (in eV) of the 19 valence and 23 Rydberg excitation energies of 5 molecules [49], calculated by the PBE and LFA-corrected PBE functionals ( $\omega = 0.15 \text{ Bohr}^{-1}$ ).

System	PBE	LFA-PBE	RILFA-PBE	LFAs-PBE
Valence (19)	0.32	0.29	0.29	0.29
Rydberg (23)	1.30	0.46	0.46	0.49

on the reaction energies of 30 chemical reactions (a test set described in Ref. [48]). As shown in Table I, the performance of the LFA-corrected PBE functionals ( $\omega = 0.15 \text{ Bohr}^{-1}$ ) is very similar to that of PBE [30]. As reaction energies are rather insensitive to the asymptote of the XC potential, our schemes do not affect the good performance of PBE.

To assess the performance of our LFA schemes on valence and Rydberg excitation energies, we perform adiabatic linear-response TDDFT calculations, using the 6-311(2+,2+)G\*\* basis set, on five molecules: nitrogen gas ( $\text{N}_2$ ), carbon monoxide (CO), water ( $\text{H}_2\text{O}$ ), ethylene ( $\text{C}_2\text{H}_4$ ), and formaldehyde ( $\text{CH}_2\text{O}$ ) on the experimental geometries taken from Ref. [49]. For computational simplicity, we adopt  $f_{x,\sigma}^{\text{LFA}}(\mathbf{r}, \mathbf{r}') = 0$  (rather than Eq. (9)) in our TDDFT calculations. For finite systems, this approximation should not make much difference in the predicted excitation energies [17]. As shown in Table II, the LFA-corrected PBE functionals ( $\omega = 0.15 \text{ Bohr}^{-1}$ ) perform well for both the valence and Rydberg excitations, while PBE severely underestimates Rydberg excitation energies due to the lack of the correct asymptote of the XC potential [30].

In conclusion, we have developed the LFA scheme, wherein an exchange density functional whose functional derivative has the correct  $(-1/r)$  asymptote can be directly added to any semilocal density functional. In contrast to semilocal density approximations, the LFA exchange kernel in reciprocal space is shown to exhibit the desirable singularity of the type  $O(-1/q^2)$ , which is an important feature for the description of excitonic effects in non-metallic solids. Applying the LFA scheme to PBE, the resulting LFA-PBE ( $\omega = 0.15 \text{ Bohr}^{-1}$ ) has yielded accurate IPs and Rydberg excitation energies for a wide range of atoms and molecules, while performing similarly to PBE for properties insensitive to the asymptote, such as reaction energies and valence excitation energies. In addition, without loss of accuracy, two closely related

schemes (RILFA and LFAs) have been developed for the efficient treatment of large systems. As the predicted results of the LFA-corrected PBE functionals are very similar, LFAs-PBE ( $\omega = 0.15 \text{ Bohr}^{-1}$ ), which has the correct ( $-1/r$ ) asymptote with essentially no added computational cost relative to PBE, is potentially very useful for the study of the frontier orbital energies, excitation energies, and time-dependent properties of large systems.

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